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STRUCTURE OF LANTHANUM-BOROGERMANATE GLASS WITH STILLWELLITE COMPOSITION ACCORDING TO VIBRATIONAL SPECTROSCOPY DATA

V. N. Sigaev,[1] S. V. Lotarev,[1] E. V. Orlova,[1] N. V. Golubev,[1] V. V. Koltashev,[2] V. G. Plotnichenko,[2] and G. A. Komandin[3]

Dielectric IR spectroscopy and Raman scattering (RS) spectroscopy have been used to confirm the presence in the structure of lanthanum-borogermanate (LBG) glass of triply coordinated boron atoms which are absent in a $LaBGe_5$ crystal. The grouping ratio $[BO_3]/[BO_4]$ is independent of the conditions under which the glass is obtained. It is proposed that amorphous nanosize regions of two types with approximately the same chemical composition but different structure are present in the glass. Regions of the first kind contain predominately quadruply coordinated boron atoms and are the basis for the formation of nuclei of stillwellite crystals, while regions of the second kind are more disordered, and a large fraction of the boron atoms in them lie at centers of oxygen triangles.

Key words: lanthanum-borogermanate glass, glass structure, structural similarity of glasses and crystals, coordination numbers, wide-band Raman scattering spectroscopy, dielectric IR spectroscopy.

Lanthanum-borogermanate glasses with compositions close to that of the ferroelectric $LaBGeO_5$ with stillwellite structure (LBG glass below) have been the objects of numerous studies for almost twenty years. This is because in these glasses it is possible to separate the $LaBGeO_5$ phase in the form of nanosize crystals [1], strong surface layers of oriented crystals [2], to obtain a quadratic optical nonlinearity in the transparent glass by means of thermal polarization [3], and to perfect crystalline textures possessing pyroelectric properties [4, 5].

In the last few years LBG glasses have become one of the most important base objects for the development of new technologies of hybrid optical materials based on controllable local crystallization of glass under the action of focused laser radiation. The laser radiation permits forming in LBG glass masses of closely spaced individual crystals with a practically monodisperse size distribution [6] and quasi-single-crystalline structure with complex geometry [7]. Thus, an entire series of promising polar glass-crystalline dielectrics can be obtained on the basis of LBG glasses with composition close to that of stillwellite. But if numerous experimental data have already been accumulated on glass formation in the LBG system and about the crystallization properties of LBG glasses, the information on their structure in the near and medium range scales is based mainly on ideas concerning the structural similarity of glasses and crystals with close compositions.

In the case of exact correspondence between the glass and crystalline phase $LaBGeO_5$, considering the ease of separating this phase in them, it is natural to suppose that short-range order in LBG glass is similar to short-range order in the crystal and that they form one and the same structural units [8]. However, data which do not fit into this model have appeared recently. In the crystal $LaBGeO_5$ coordination number of all boron atoms is 4, while according to the nuclear magnetic resonance (NMR) data [1] about half the boron atoms in LBG glass lie at the centers of triangles. This fact contradicts the principle of crystallochemical similarity, formulated and experimentally confirmed initially for one-component glasses (SiO_2, B_2O_3, P_2O_5) [9] and remaining fundamental in the theoretical assessment of short-range order structure in multicomponent glasses, for which reliable experimental data on the interatomic distances and the coordination numbers (CNs) are very difficult to obtain.

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[1] Center for Optical Glass at the D. I. Mendeleev Russian Chemical-Technology University, Moscow, Russia.
[2] Scientific Center for Fiber Optics of the Russian Academy of Sciences, Moscow, Russia.
[3] A. M. Prokhorov Institute of General Physics of the Russian Academy of Sciences, Moscow, Russia.
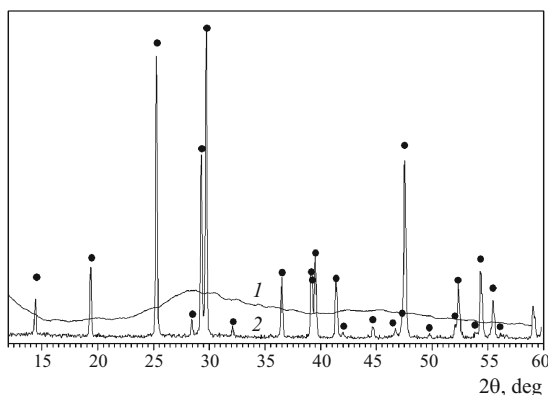
Fig. 1. X-ray diffraction pattern of the glass $25La_2O_3 – 25B_2O_3 – 50GeO_2$ (*1*) and the crystalline powder $LaBGeO_5$ (*2*). The peaks indicated correspond to $LaBGeO_5$ reflections (card No. 77-0721 JCPDS).
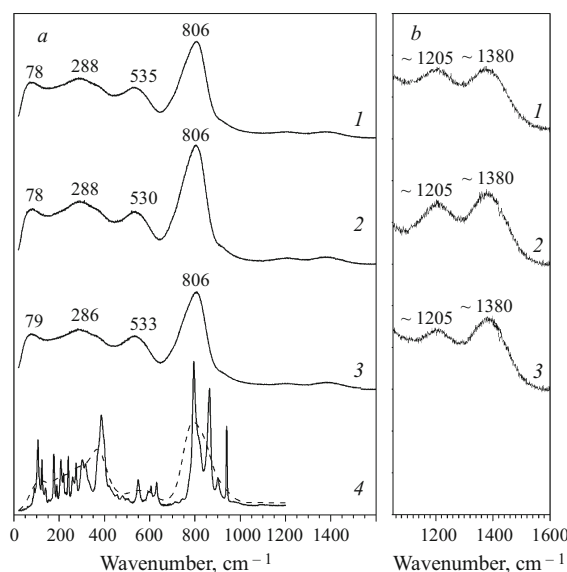

Fig. 2. Wide-band (*a*) and high-frequency (*b*) sections of the RS spectrum of crystalline powder of $LaBGeO_5$ and the glass $25La_2O_3 \cdot 25B_2O_3 \cdot 50GeO_2$ obtained by different methods: *1*) founding from mix at 1300°C; *2*) founding from mix at 1500°C; *3*) melting of crystalline $LaBGeO_5$ into glass at 1220°C; *4*) crystalline powder $LaBGeO_5$ (dashed line) convolution of the RS spectrum of the crystal and a Gaussian function).

In the present work we have obtained LBG glass with the composition of stillwellite $LaBGeO_5$ and investigated their structure by means of wide-band Raman scattering (RS) spectroscopy and dielectric IR spectroscopy using the procedures describe previously in [10].

To trace the changes of the ratio BO_3 / BO_4 as a function of the thermal history of the sample the glasses were obtained from chemically pure $La(OH)_3$, H_3BO_3, and GeO_2 in a platinum crucible by two methods:

– melting the mix at two substantially different temperatures 1300 and 1500°C in 30 min and pressing the melt between steel plates;

– remelting in glass of $LaBGeO_5$ crystalline powder at 1200°C near the melting point of $LaBGeO_5$; crystalline $LaBGeO_5$ powder was obtained by means of solid-phase reactions: heat-treatment of pressed pellets from the above-indicated reagents at 1100°C for 30 h; to obtain glass with a prescribed composition, losses due to evaporation of B_2O_3 were taken into account by weighing the mix and crucible before and after melting.

X-ray phase analysis (XPA) was performed with a DRON-3M diffractometer using powder samples. The RS spectra were recorded in the frequency range $20 – 1850$ cm^{-1} using a T64000 (Jobin Ivon) triple spectrograph; excitation of scattering was accomplished by means of the green line 514.5 nm of a Stabilite 2017 (Spectra Physics) Ar laser. The dielectric spectra of the imaginary part ε'' of the permittivity were obtained by combining complementary measurements performed by precision monochromatic submillimeter spectroscopy using backward-wave tubes and reflective IR spectroscopy. The spectra of complex transmission at frequencies $3 – 30$ cm^{-1} (Epsilon submillimeter spectrometer) and reflection in the range $20 – 4000$ cm^{-1} (Bruker IFS-113v IR Fourier spectrometer) were measured. To calculate the spectra of the imaginary part ε'' of the permittivity the spectra obtained were processed together by dispersion analysis and the Kramers – Kronig method.

The x-ray phase analysis of powder obtained by solid-phase synthesis confirmed that this powder consists of a single phase corresponding precisely to $LaBGeO_5$ (card No. 77-0721 from the JCPDS x-ray data base). The x-ray diffraction pattern of the LBG glass sample (Fig. 1) does not contain Bragg peaks, confirming that the glass is completely amorphous and does not contain a crystalline phase.

Figure 2 shows unpolarized wide-band RS spectra of LBG glasses with different thermal history. The figure also displays the unpolarized RS spectrum obtained for $LaBGeO_5$ crystalline powder as well as the result of the convolution of this spectrum with a Gaussian function (FWHH — 75 cm^{-1}) as the spectrum of an "artificially disordered" crystal. The latter curve is illustrative only and is presented as an additional graphic method of comparing with the spectrum of the glass.

Figure 3 shows wide-band dielectric IR spectra of LBG glasses, calculated by dispersion analysis (the spectra calculated by the Kramers – Kronig method turned out to be very close to the results of dispersion analysis). In reality, the IR spectra of the glasses were measured to frequency 4000 cm^{-1}, while the RS spectrum of the glass samples was measured to 1850 cm^{-1}, but above 1600 cm^{-1} the RS signal of the experimental samples is zero and gives no additional information, and the vibrational resonances of the atomic bonds present in glass with this composition lie below this value. For this reason, the plots in Fig. 3 are bounded by the value 1600 cm^{-1} in order to obtain a clearer representation of the data.
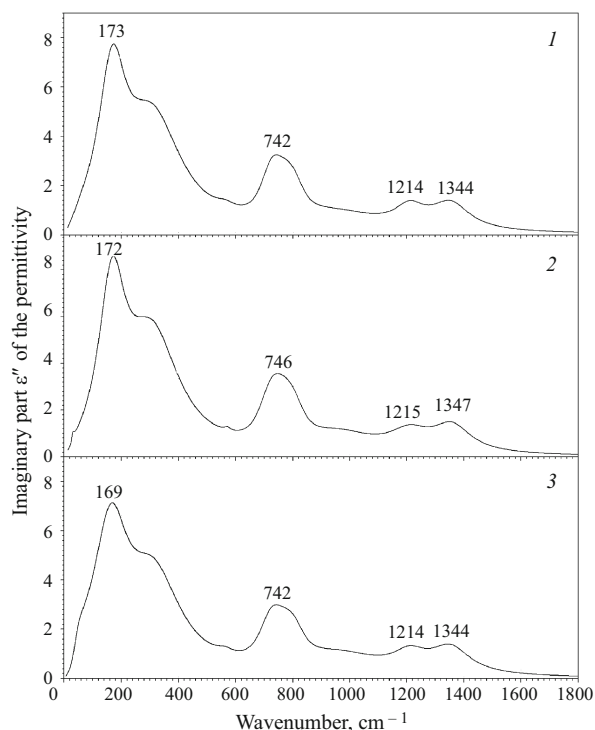
Fig. 3. Dielectric IR spectra ε'' of the glass $25La_2O_3 \cdot 25B_2O_3 \cdot 50GeO_2$ and the RS spectra of the glass $25La_2O_3 \cdot 25B_2O_3 \cdot 50GeO_2$ obtained by different methods: *1*) founding from mix at 1300°C; *2*) founding from mix at 1500°C; *3*) melting of crystalline $LaBGeO_5$ into glass at 1220°C.

According to the spectroscopic data for the crystal $LaBGeO_5$ [11] the intense bands in the region $800 - 900 \text{ cm}^{-1}$ (RS) and $700 - 800 \text{ cm}^{-1}$ (IR) correspond to stretching vibrations of $[GeO_4]$ tetrahedra with a small contribution of vibrations of $[BO_4]$ tetrahedra; the latter in the spectrum of the glass are completely masked by the broadened intense peak due to $[GeO_4]$. For the crystal the weak bands in the region $500 - 700 \text{ cm}^{-1}$ characterize bending-stretching vibrations of chains of $[BO_4]$ tetrahedra.

The very close similarity between the RS spectra of glasses in Fig. 2 and at least as good similarity of the IR spectra in Fig. 3 show that irrespective of the founding temperature practically the same structure is formed in the LBG glass. This result extends to the coordination of the boron atoms. According to Efimov's data [12] the bands in the high-frequency region ($1150 - 1500 \text{ cm}^{-1}$) of the RS spectrum (see Fig. 2b) and the IR spectrum (see Fig. 3) correspond to the vibrations of $[BO_3]$ triangles. There are no resonances in this frequency range of other groups in glass with this composition, so that the appearance of resonances with such frequencies unequivocally attests to the presence of triply coordinated boron in the structure of the glass. This agrees well with the NMR data presented above [1]. The comparatively low intensity of the bands in the RS spectrum, which correspond to triply coordinated boron, is due to selection rules, according to which these vibrations should not ap-

pear in the Raman scatter, but because of the disordering of the structure of the glass this rule breaks down partially, and negligible scattering is still present. The high-frequency bands of the IR spectrum which are allowed by the selection rules have an appreciable intensity. Unfortunately, it is difficult to determine quantitatively the ratio $[BO_3]/[BO_4]$ of the structural units from the spectroscopic data.

The transition $[BO_4] \rightarrow [BO_3]$ is associated with a change of the character of the bands in the region $500 - 700 \text{ cm}^{-1}$ where an appreciable peak appears; this peak is most likely due to the deformation vibrations of the triangles $[BO_3]$, while the intense bands at $300 - 450 \text{ cm}^{-1}$ correspond to vibrations of the tetrahedra $[GeO_4]$.

The high-frequency peaks in the IR spectra and the RS spectra in the range $1150 - 1450 \text{ cm}^{-1}$ remain practically unchanged from one sample to another. Therefore, the same short-range order structure, characterized by the formation of crystals during melting or triangular groups $[BO_3]$, whose number is the same, as the melt cools, forms in the glass irrespective of the thermal history of founding. Taking account of the precision NMR data [1], it can be supposed that in all three glasses made at 1300 and 1500°C or consisting of the remelted crystal $LaBGeO_5$, the fraction of $[BO_3]$ crystals is of the order of $50 - 60\%$.

It is interesting that the RS spectrum of glass at frequencies below 1100 cm^{-1} is very close to the "disordered" spectrum of the crystal $LaBGe_3$, with the exception of only the low-frequency region ($< 200 \text{ cm}^{-1}$) where the so-called "boson" peak (maximum at 78 cm^{-1}), present in the RS spectra of any glass irrespective of the composition, makes a substantial contribution to the spectrum of glass. Such similarity points to the presence of structural closeness of the glass and crystal at the short-range order level. However, the above-proved existence of boron atoms with coordination number 3 in large numbers in the same glasses seems, at first glance, to contradict the supposition just made.

This contradiction can be eliminated in a model where the initial LBG glass consists of more ordered ("crystal-similar") fragments, structurally similar on the short- and long-range scales with stillwellite $LaBGe_5$ (and containing only or almost only tetrahedral coordinated boron atoms), and nanoregions where a substantial part of the boron (more than half) has a coordination number 3. Since it is assumed that in these nanoregions the fragments of three networks mix together — $[BO_3]$, $[BO_4]$, and $[GeO_4]$ — in the absence of structural correspondence to the crystal analogue, it is natural to suppose that they are comparatively strongly disordered as compared with the stillwellite-like regions, where $[BO_4]$ tetrahedra predominate. It should be noted once again that the "crystal-like" regions containing only quadruply coordinated boron are also completely amorphous (see Fig. 1).

It is very difficult to establish whether these two types of regions, comprising LBG glass, differ only by structure or also by chemical composition. However, it clear from the

data presented above that the nano nonuniform structure of LBG glass is formed in the melt. For this reason, the fluctuations in the chemical composition between the regions with different structure are either absent or negligible. They are fixed during cooling, creating in the glass the same nanostructure irrespective of the cooling rate and the founding temperature.

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